Fundamentals and Application of Chemical Solution Techniques for Thin Films Synthesis

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Thin Film Deposition (extrinsic)

Physical Vapor Deposition (PVD) - Film is formed by atoms directly transported from source to the substrate through gas phase
  • Evaporation
    • Thermal evaporation
    • E-beam evaporation
  • Sputtering
    • DC sputtering
    • DC Magnetron sputtering
    • RF sputtering
    • Reactive PVD

Chemical Vapor Deposition (CVD) - Film is formed by chemical reaction on the surface of substrate
  • Low-Pressure CVD (LPCVD)
  • Plasma-Enhanced CVD (PECVD)
  • Atmosphere-Pressure CVD (APCVD)
  • Metal-Organic CVD (MOCVD)

Chemical Solution Deposition (CSD) – Film is formed starting from a liquid film

Platting
General Characteristics of Thin Film Deposition

- Deposition Rate
- Film Uniformity
  - Across wafer uniformity
  - Run-to-run uniformity
- Materials that can be deposited
  - Metal, Ceramic, Polymer
- Quality of Film – Physical and Chemical Properties
  - Stress, Adhesion, Stoichiometry, Film density, pinhole density, Grain size, boundary property, and orientation, Breakdown voltage, Impurity level
- Deposition Directionality
  - Directional: good for lift-off, trench filling
  - Non-directional: good for step coverage
- Cost of ownership and operation
CVD Reactors

1.) Atmospheric Pressure CVD (APCVD)
Advantages: High deposition rates, simple, high throughput
Disadvantages: Poor uniformity, purity is less than LPCVD
Used mainly for thick oxides.

2.) Low Pressure CVD (LPCVD at ~0.2 to 20 torr)
Advantages: Excellent uniformity, purity
Disadvantages: Lower (but reasonable) deposition rates than APCVD
Used for polysilicon deposition, dielectric layer deposition, and doped dielectric deposition.

3.) Metal Organic CVD (MOCVD)
Advantages: Highly flexible—> can deposit semiconductors, metals, dielectrics
Disadvantages: HIGHLY TOXIC!, Very expensive source material. Environmental disposal, costs are high.

4.) Plasma Enhance CVD. PE-MOD (Metal Organic Decomposition)
Plasmas are used to force reactions that would not be possible at low temperature.
Advantages: Uses low temperatures necessary for rear end processing.
Disadvantages: Plasma damage typically results.
Used for dielectrics coatings.
## Chemical Solution Deposition (CSD) Processes

CSD collects all the processes that the precursor and the deposited film are liquid.

### Five basic steps

<table>
<thead>
<tr>
<th>Step</th>
<th>State</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of the precursor solution</td>
<td>Liquid solution</td>
<td>RT</td>
</tr>
<tr>
<td>Deposition on a substrate</td>
<td>Liquid film</td>
<td>RT</td>
</tr>
<tr>
<td>Drying film</td>
<td>Hybrid amorphous film</td>
<td>100-200°C</td>
</tr>
<tr>
<td>Burning of organic species</td>
<td>Porous amorphous film</td>
<td>280-390°C</td>
</tr>
<tr>
<td>Densification and crystallization</td>
<td>Dense crystalline film</td>
<td>450-850°C</td>
</tr>
</tbody>
</table>
Precursor Solution

The Preparation of multioxides materials precursor solution, such as perovskites, involves the use of cation compounds that are dissolved in a common solvent.

Several processes can be used for precursor solution preparation.

Each process gives one characteristic precursor that exhibit dramatic effect on the film properties.

Simple processes consist in mixing soluble metal compounds in a common solvent where the precursor species retain a strong resemblance to the starting.

More complex processes are similar to a engineering molecular, tendering to synthesize precursors with structures similar to the final crystal structure of the desired perovskite film.
FUNDAMENTALS OF THE SOL-GEL

**Hydrolysis**

\[ M(OR)_n + H_2O \rightarrow HO - M(OR)_{n-1} + HOR \]

**Condensation: (water elimination)**

\[ (RO)_{n-1}M - OH + HO - M(OR)_{n-1} \rightarrow (RO)_{n-1}M - O - M(OR)_{n-1} + H_2O \]

**Oligomerization**

\[ (RO)_{n-1}M - O - \overset{(OR)_{n-2}}{M} - O - \overset{(OR)_{n-2}}{M} - O - \overset{(OR)_{n-2}}{M} - M(OR)_{n-1} \]

**FORMATION OF THE GEL NETWORK**
Characteristics SG process

- High water sensitive starting material
- Chemical bonding
- Different reaction ratio of metal precursors
- Poor control of molecular structure
- From lineal chain to 3-dimensional network
- Porous films
- Unstable solution
- High shrinkage
**Sol-Gel Process: 2- methoxyethanol Route**

**Lead Precursor, Alcohololisis**

\[ Pb(OAc)_2 \cdot 3H_2O + MeOEtOH \rightarrow Pb(\text{OEtOMe})_{2-x}(OOCH)_3 \]

**Zirconium and Titanium Precursors, Alcohol exchange**

\[ Zr(\text{OPr}^n)_4 + 4\text{MeOEtOH} \rightarrow Zr(\text{OEtOMe})_4 + 4\text{HOPr}^n \]
\[ Ti(OEt)_4 + 4\text{MeOEtOH} \rightarrow Ti(\text{OEtOMe})_4 + 4\text{HOEt} \]

- **Lead Acetate Trihydrate + 2 Methoxyethanol**
  - Dehydration and alcoholysis (10 hs, 124 ºC)
  - Lead precursor (X)

- **Zirconium n-Propoxide + 2-Methoxyethanol**
  - Alcohol Exchange (4 hs, 124 ºC)
  - Zirconium precursor (Y)

- **Titanium Ethoxide + 2-Methoxyethanol**
  - Alcohol Exchange (5 h, 124 ºC)
  - Titanium precursor (Z)

**Complexation** (124 ºC, 3 h)

**PZT PRECURSOR (W)**

- **Common alkoxide group**
- **High water sensitive starting material**
- **Multi-metallic alkoxide**
- **Precursor structure resembles to the PZT perovskite lattice**
Modified Sol-Gel Process

Chelating agents: HOOCCH₃ (Acetic acid) OR 2-4-pentanedione (ACAC)

Zirconium and Titanium Precursors

\[ Ti(OEt)₄ + HOAc \rightarrow Ti(OPrⁿ)_{4-x}(OOCCH₃)ₓ \]
\[ Zr(OPrⁿ)₄ + HOAc \rightarrow Zr(OPrⁿ)_{4-x}(OOCCH₃)ₓ \]

Lead Precursor \( Pb(OAc)₂ \cdot 3H₂O \)

SIMILAR PROCESS
LESS REACTIVITY
LESS STRUCTURE CONTROL

Metal-Organic Decomposition: MOD

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Solvent</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long chain caboxylate</td>
<td>M(OOCCₙHₙ₊₁)</td>
<td>Xilene</td>
</tr>
<tr>
<td>Short chain</td>
<td>M(OOCCₙHₙ₊₁)</td>
<td>Alcohol</td>
</tr>
</tbody>
</table>
Chelate route

Starting materials

• Chelating agents: Diethanolamine, Triethanolamine, 3-Hydroxy-2-butanone (Acetoin).
• (n-1) or (n-2) non hydrolyzing metal precursor soluble in alcohol. Nitrates or acetates.
• One or two metal alkoxides.
• Short chain alcohol solvent

• Low temperature burning residual organic groups (<450 °C).
• Very low content of hydroxyls residual
• Onset of crystallization at lower temperature
### PROCESSES FOR PRECURSOR SOLUTION PREPARATION

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>Simplicity</th>
<th>Reactivity reactants</th>
<th>Organic residue Shrinkage</th>
<th>Structure control</th>
<th>Other Parameter control</th>
<th>Stable precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrates</td>
<td>Very High</td>
<td>None</td>
<td>Very low</td>
<td>None</td>
<td>None</td>
<td>Very high</td>
</tr>
<tr>
<td>Citrate/Nitrate</td>
<td>Very High</td>
<td>None</td>
<td>Very low</td>
<td>None</td>
<td>None</td>
<td>High</td>
</tr>
<tr>
<td>Pechini/Nitrate</td>
<td>High</td>
<td>Low</td>
<td>None</td>
<td>Thickness Texture</td>
<td>None</td>
<td>High</td>
</tr>
<tr>
<td>MOD</td>
<td>Medium</td>
<td>Low</td>
<td>Very High</td>
<td>None</td>
<td>Thickness Texture</td>
<td>High</td>
</tr>
<tr>
<td>Chelate route</td>
<td>Medium</td>
<td>Low</td>
<td>Very Low</td>
<td>Low</td>
<td>Thickness Texture</td>
<td>High</td>
</tr>
<tr>
<td>Modified Sol-gel</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Thickness Texture</td>
<td>Low</td>
</tr>
<tr>
<td>Sol-gel</td>
<td>Very low</td>
<td>Very high</td>
<td>Medium</td>
<td>High</td>
<td>Thickness</td>
<td>Very low</td>
</tr>
</tbody>
</table>
DIP COATING

\[ t_l \propto \left( \frac{V \mu}{\rho g} \right)^n \]
**SPIN COATING**

**Step 1:** is the deposition of the coating fluid onto the wafer or substrate.

**Step 2:** the substrate is accelerated up to its final rotation speed. Aggressive fluid expulsion from the wafer.

**Step 3:** the substrate is spinning at a constant rate and fluid viscous forces dominate fluid thinning behaviour. Possible starting of evaporation for volatile solvent.
SPIN COATING PARAMETERS

- Solution viscosity
- Solid content
- Angular speed
- Spin Time
SPIN COATING DEFECTS

**Film too thin**
Spin speed too high. Select lower speed  
Spin time too long. Decrease time during high speed step  
Inappropriate precursor solution

**Film too thick**
Spin speed too low. Select higher speed  
Spin time too short. Increase time during high speed step  
Inappropriate precursor solution. To dilute solution
Air bubbles on wafer surface
Air bubbles in dispensed fluid
Dispense tip is cut unevenly or has burrs or defects

Comets, streaks or flares
Fluid velocity (dispense rate) is too high
Spin bowl exhaust rate is too high
Resist sits on wafer too long prior to spin
Spin speed and acceleration setting is too high
Particles exist on substrate surface prior to dispense
Fluid is not being dispensed at the center of the substrate surface
**Swirl pattern**
Spin bowl exhaust rate is too high
Fluid is striking substrate surface off center
Spin speed and acceleration setting is too high
Spin time too short

**Uncoated Areas**
Insufficient Dispense Volume.
Non uniform wetting

**Pinholes**
Air bubbles
Particles in fluid. Solution filtration
Particles exist on substrate surface prior to dispense. Substrate cleaning
As-prepared film

Low porous Amorphous Film

Physical gel film

High porous Amorphous Film

Chemical gel film
Densification and Crystallization

The film microstructure and orientation depends from:

- The substrate and Solution chemistry,
- Material composition and crystallization path
- Sequence and temperatures of the thermal treatment.
Densification

Mechanisms of Sintering
- Condensation Reaction
- Structural relaxation
- Viscous flow
- Solid state reaction

<table>
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<tr>
<th>HEATING RATE</th>
<th>Sintering Mechanics</th>
<th>Densification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>Consecutive</td>
<td>Lower</td>
</tr>
<tr>
<td>High</td>
<td>Concurrent</td>
<td>Higher</td>
</tr>
</tbody>
</table>
Phase transition
The diagram illustrates the concept of a spinodal point in a system. The second derivative of the free energy with respect to the order parameter is:

\[ \frac{\partial^2 G}{\partial x^2} > 0 \]

This indicates a region of metastable equilibrium, where the system is stable against small perturbations. The graph shows the free energy profile with the spinodal point at \( \frac{\partial^2 G}{\partial x^2} = 0 \), beyond which the system becomes unstable.

The left side of the diagram highlights the concept of metastable equilibrium, with the center of mass required to overcome metastability.

The right side shows the transition to unstable equilibrium, indicated by the negative second derivative.

In summary, the diagram illustrates the transition from metastable to unstable equilibrium through the spinodal point.
Crystallization

Film crystallization in solution-derived thin films performs by a **nucleation-and-growth** process. The theoretical picture is parallel to that of glasses crystallization.

Path A:  \[ \Delta G_{a\rightarrow c} \]
\[ \text{Amorh } \rightarrow \text{ Ferroel} \]

SrTiO\(_3\) amorph \(\rightarrow\) SrTiO\(_3\) Feroel

Path B:  \[ \Delta G_{a\rightarrow i} \quad \Delta G_{i\rightarrow c} \]
\[ \text{Amorh } \rightarrow \text{ Interd } \rightarrow \text{ Ferroel} \]

PZT amorph \(\rightarrow\) Pyrochlore \(\rightarrow\) PZT perovkite
Nucleation

Volume free energy change ($\Delta G_{a\rightarrow c}$) drives nucleus growth. Surface energy, $\Delta G_S$ counter-drives

$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_{a\rightarrow c} + 4\pi r^2 \gamma$$

$\gamma$: interfacial energy crystalline – amorphous,

$$r^* = -\frac{2\gamma}{\Delta G_{a\rightarrow c}}$$

$$\Delta G^* = \frac{16}{3} \frac{\pi \gamma}{\Delta G_{a\rightarrow c}}$$
\[ \Delta G = n_r \Delta G_r - T \Delta S_C \]

\[ \Delta S_C = k \ln \frac{(n_0 + n_r)!}{n_0!n_r!} \]

\[ \Delta G = n_r \Delta G_r - kT \ln \frac{(n_0 + n_r)!}{n_0!n_r!} \]

\[ \left( \frac{\partial G}{\partial n_r} \right)_T = 0 \]

\[ -\Delta G_r = kT \ln \left( \frac{n_r}{n_0 + n_r} \right) \quad kT \ln \left( \frac{n_r}{n_0} \right) \]

\[ \frac{n_r}{n_0} = \exp \left( -\frac{\Delta G_r}{kT} \right) \]
Homogeneous vs Heterogeneous Nucleation

\[ \cos \theta = \frac{\gamma_{Sa} - \gamma_{Sc}}{\gamma_{ac}} \]

\( \theta \): contact angle

\( \gamma_{Sa} \): substrate – amorphous interfacial energy

\( \gamma_{Sc} \): substrate – crystalline interfacial energy

\( \gamma_{Sa} \): amorphous – crystalline interfacial energy

\[ \Delta G_{HETE}^* = f(\theta) \Delta G_{HOMO}^* \]

\[ f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \]

0° ≤ \( \theta \) ≤ 180°  \hspace{1cm} 1 ≥ \cos \theta ≥ -1  \hspace{1cm} 0 ≤ f(\theta) ≤ 1

Full wetting \hspace{1cm} \theta = 0 \hspace{1cm} f(\theta) = 0 \hspace{1cm} \Delta G_{HETE}^* = 0

No wetting \hspace{1cm} \theta = 180° \hspace{1cm} f(\theta) = 1 \hspace{1cm} \Delta G_{HETE}^* = \Delta G_{HOMO}^*
Nucleation rate

\[ \nu = \nu_0 \exp\left(-\frac{E_a}{kT}\right) \]

Collision frequency at interface nucleus, 
\( E_a \): atomic movement activation energy

\[ N = \nu_0 n_0 n_s \exp\left(-\frac{\Delta G^*}{kT}\right) \exp\left(-\frac{E_a}{kT}\right) \]
Effects of the Heat Treatment on the Nucleation

<table>
<thead>
<tr>
<th>RATE</th>
<th>Favors Nucleation</th>
<th>Rate of Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>&lt; 100 °C/min</td>
<td>At low Temperature</td>
</tr>
<tr>
<td>RTA</td>
<td>&gt; 1000 °C/min</td>
<td>At high Temperature</td>
</tr>
</tbody>
</table>
PROBLEM
In ferroelectric capacitors built with films of BaTiO$_3$ (BT), PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (PZT) and SrBi$_2$Ta$_2$O$_9$ (SBT) and electrode Pt. What heat treatment would develop the appropriate microstructure that produce the maximum remanent polarization.

PATHS
- BT: Amorphous $\rightarrow$ BT crystalline
- PZT: Amorphous $\rightarrow$ pyrochlore $\rightarrow$ PZT crystalline
- SBT: Amorphous $\rightarrow$ Fluorite SBT $\rightarrow$ perovskite SBT
INTERACCIÓN FILM-SUBSTRATE

Interdiffusion

Structural effect

Thermal Activated Process

\[ \nu \propto \exp \left( - \frac{E_a}{RT} \right) \]
Lead less Ferroelectrics

\((K_xNa_{1-x})NbO_3\) (NKN)

**EFECTO DE LA TEMPERATURA**

- **NKN**
- **Pt**
- Por indentificar

![Graph showing effects of temperature](image)

- **200**
- **002**

Solución precursora de Niobio

- Acetoin + Etanol

Solución (Na_{0.50}K_{0.50})NbO_3 (NKN)

Solución precursora de Niobio

- Solución
- H_2O
- HCl